REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Papers	

4. TITLE AND SUBTITLE

Please see attached

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M2C8

5f. WORK UNIT NUMBER
345709

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
Please see attached

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Leilani Richardson
Unclassified	Unclassified	Unclassified	A		19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015

2303MCP

MEMORANDUM FOR PRS (In-House Contractor Publication)

FROM: PROI (STINFO) 17 May 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-116** Jerry Boatz (PRSP) et al., "First Principles Calculation of the Chemisorption Properties of Nitro-containing Molecules on the Al(111) Surface (Multiscale Simulations of High Energy Density Materials Challenge Project)" (Viewgraphs)

DoD Users Group Conference **(Statement A)**
(Austin, TX, 10-14 June 2002) **(Deadline: 07 June 2002)**

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
Comments:_____

Signature _____ Date _____

2. This request has been reviewed by the Public Affairs Office for: a.) appropriateness for public release and/or b) possible higher headquarters review.
Comments: _____

Signature _____ Date _____

3. This request has been reviewed by the STINFO for: a.) changes if approved as amended, b) appropriateness of references, if applicable; and c.) format and completion of meeting clearance form if required
Comments:_____

Signature _____ Date _____

4. This request has been reviewed by PR for: a.) technical accuracy, b.) appropriateness for audience, c.) appropriateness of distribution statement, d.) technical sensitivity and economic sensitivity, e.) military/ national critical technology, and f.) data rights and patentability
Comments:_____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

_____

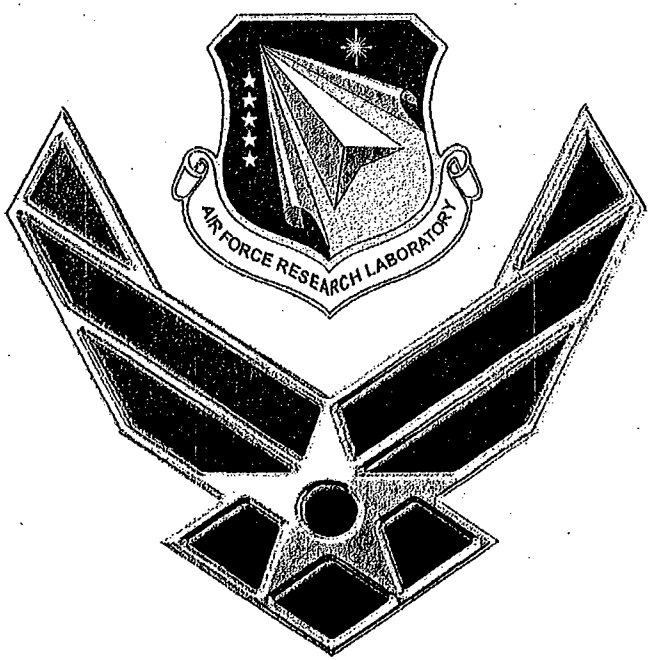
PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division

CC 02-116

First Principles Calculations of ction of Nitro Compounds with the Al (111) Surface

DoD UGC, 10-14 Jun 02

Austin, TX



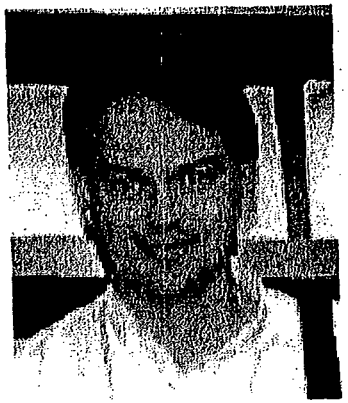
Jerry Boatz

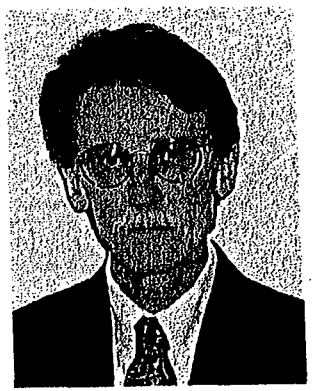
Senior Research Chemist

Propulsion Directorate

Air Force Research Laboratory

Multiscale Simulations of High Energy Density Materials (MSoH) Challenge Project





Dan C. Sorescu* **Jerry Boatz**** **Donald L. Thompson*****

* National Energy Technology Laboratory, Pittsburgh, PA 15236

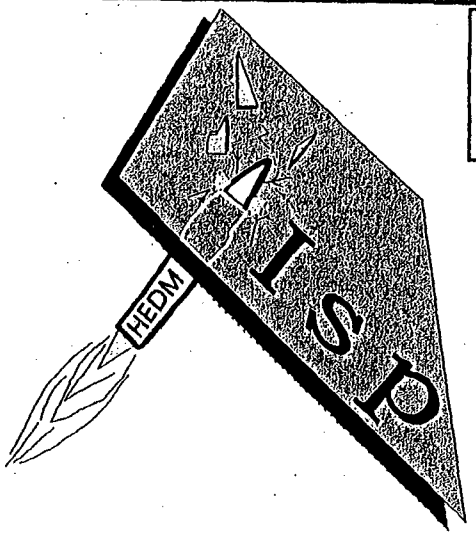
** Air Force Research Laboratory, Edwards AFB, CA 93524

*** Oklahoma State University, Dept. of Chemistry, Stillwater, OK 74078

OUTLINE

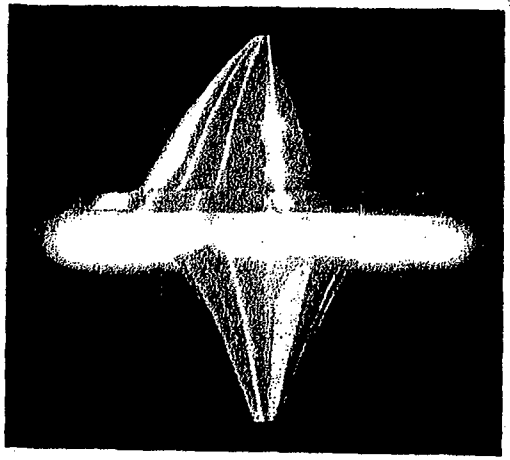
1. Introduction
   - Background on HEDM
   - Payoffs
2. Theoretical Methods and benchmarks
   - Plane-wave DFT
   - Molecular Dynamics
3. Results
4. Summary

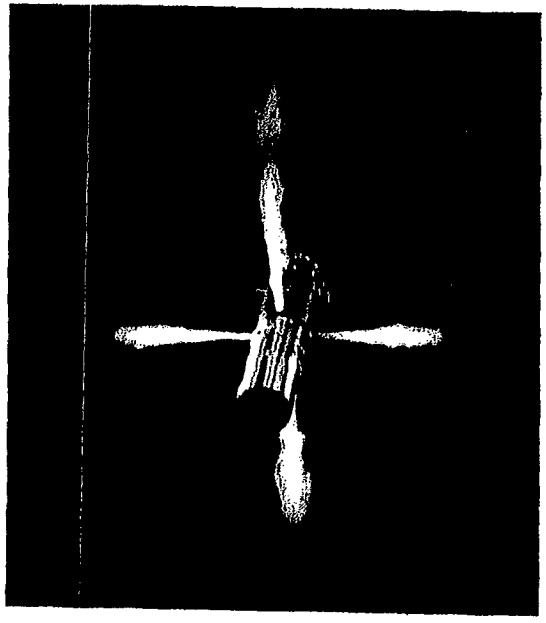
What We Are Trying To Do

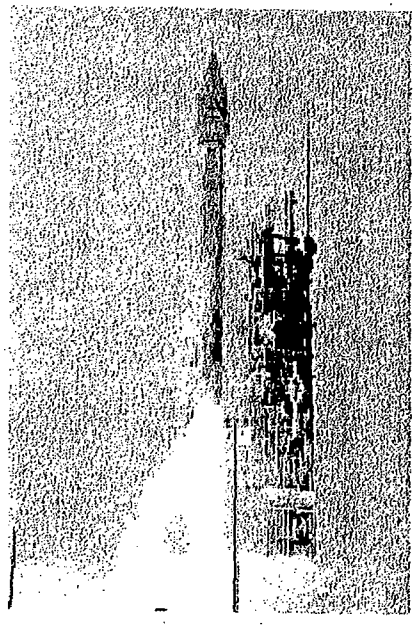


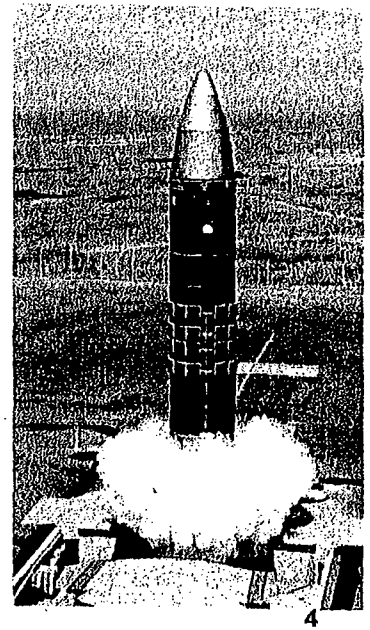
Identify, develop, and transition new propellants and advanced concepts for propulsion applications

- Hydrocarbon fuels for liquid boost
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for spacecraft and upper stages
- Cryogenic propellants for upper stages
- Laser lightcraft for microsatellite and other applications









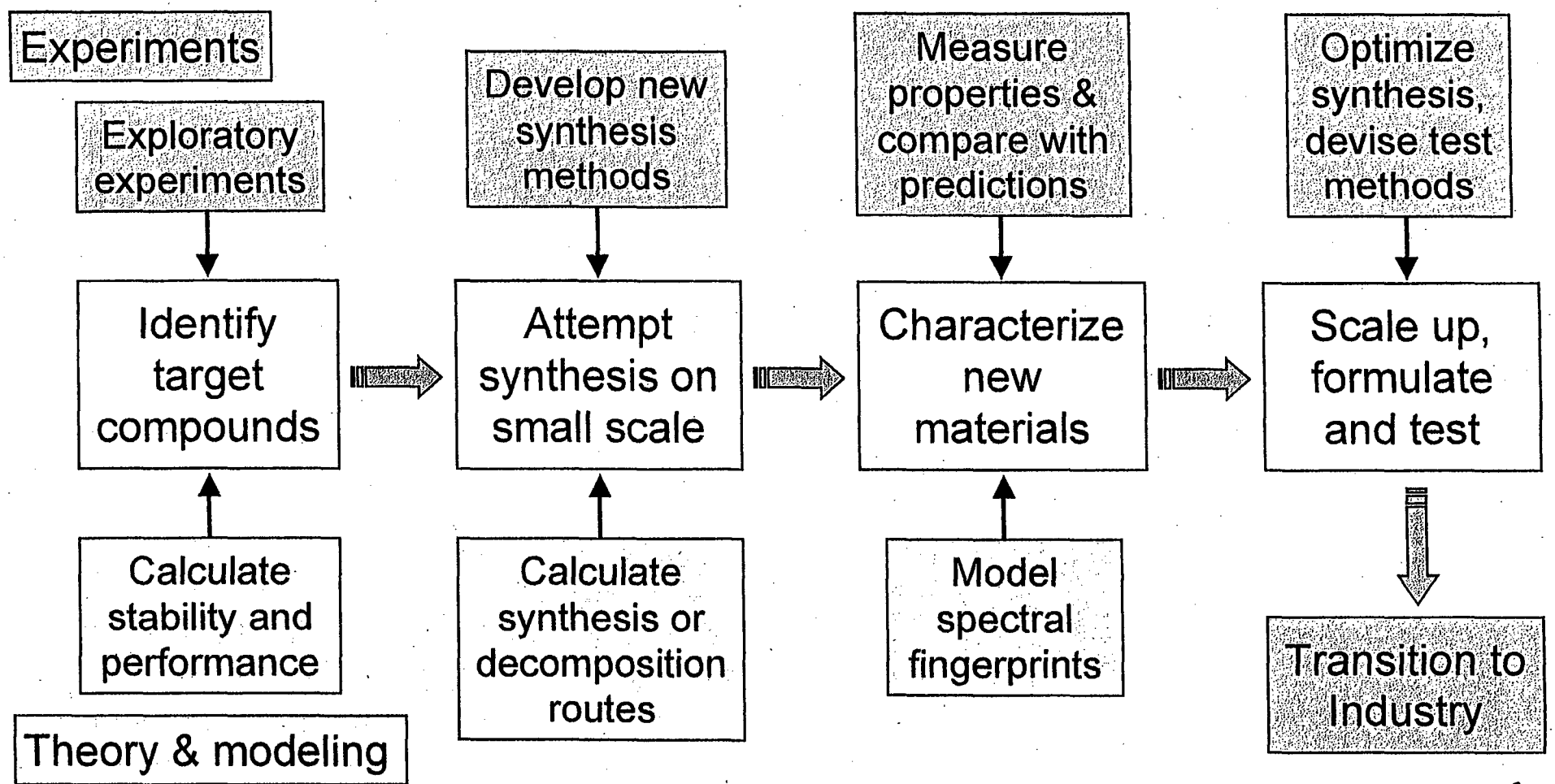
What Difference It Will Make

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas II // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 **(+25%)**
SSTO RLV	Lockheed SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 **(+70%)**
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 **(+49%)**

Our research is aimed at increasing propellant Isp by as much as 50%

How We Do What We Do
Propellant Discovery & Development

Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics



MSoH: Concept

Atomistic level understanding of condensed phase properties of energetic materials

- which factors influence the phase transitions (e.g., the melting point of energetic crystals?
- what is the mechanism of phase stabilization in AN salts?
- how are the chemical properties of energetic materials influenced by chemisorption on metallic surfaces?

Technical tasks include

a) Characterization of static, dynamic properties of AN, ADN salts
   - structural, thermodynamic, transport properties and phase transitions

b) Investigation of KNO_3-induced phase stabilization of ammonium nitrate (AN) salts

c) Interactions between HEDM molecules and Al surfaces, nanoclusters.
   - how do surface/cluster interactions modify the chemical properties of HEDM?
   - RDX, HMX, FOX-7 (1,1-diamino-2,2-dinitroethylene)

Objectives of the Current Computational Research Program

To identify the chemisorption mechanism of various nitro compounds on Al surface.

Particular important goals:

a) to clarify if dissociative chemisorption can take place;

b) what type of species or radicals are formed on the surface.

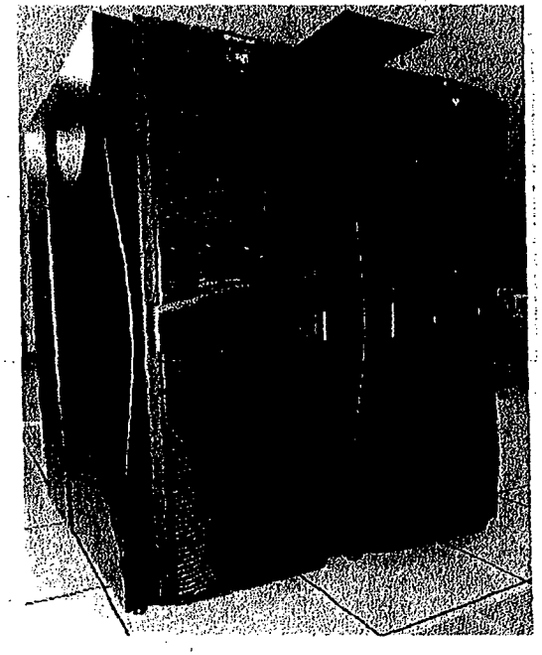
Limitations: temperature effects are not considered in the present set of calculations.

Computational Method :
Ab Initio Total Energy Calculations

- Theoretical approach: spin polarized DFT with GGA and pseudopotential method.
- The occupied electronic orbitals are expanded in a plane-wave basis $\Psi_i(r) = \sum_G c_{iG} \exp(iGr)$ with reciprocal lattice vectors G limited by $\frac{\hbar^2 G^2}{2m} < E_{cut}$, Ecut: 396 eV

  Exchange-Correlation Functionals: PW91
- Pseudopotentials: Ultrasoft Vanderbilt-type
- K-point sampling: Monkhorst-Pack Special K-pts
- Electron Smearing Near Fermi Level with Extrap.to T=0
  VASP: Methfessel-Paxton Function, 0.1 eV min. width.

VASP: "Vienna Ab Initio Simulation Package",
J. Haffner, G. Kresse et al., Univ. of Vienna

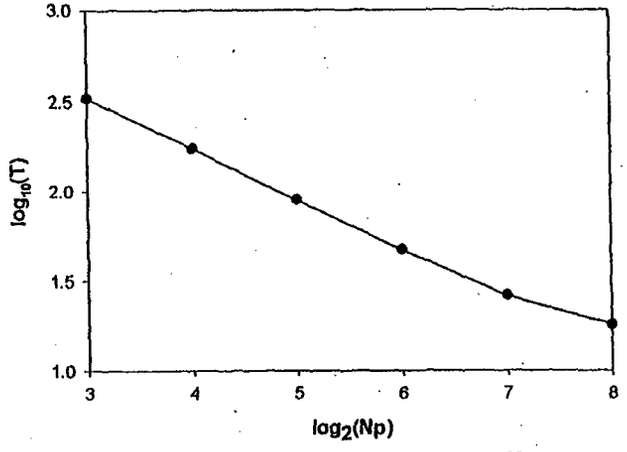


DOD HPC
ARL MSRC and NAVO MSRC

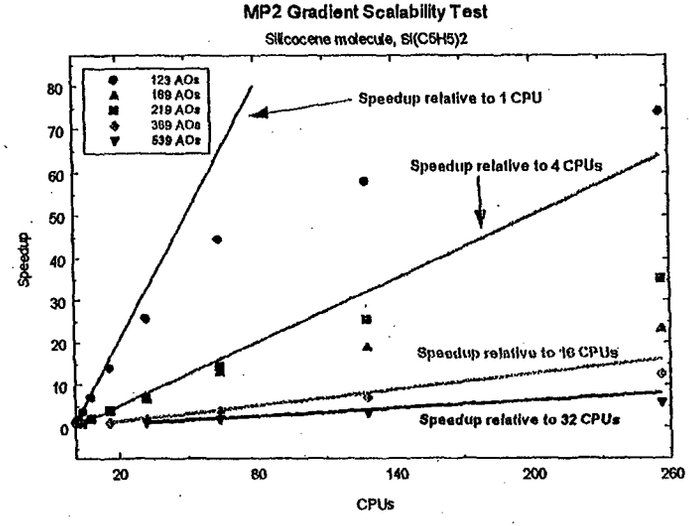
MSoH: Scalable CCM Software

DL_POLY_2.0

Run on Cray T3E

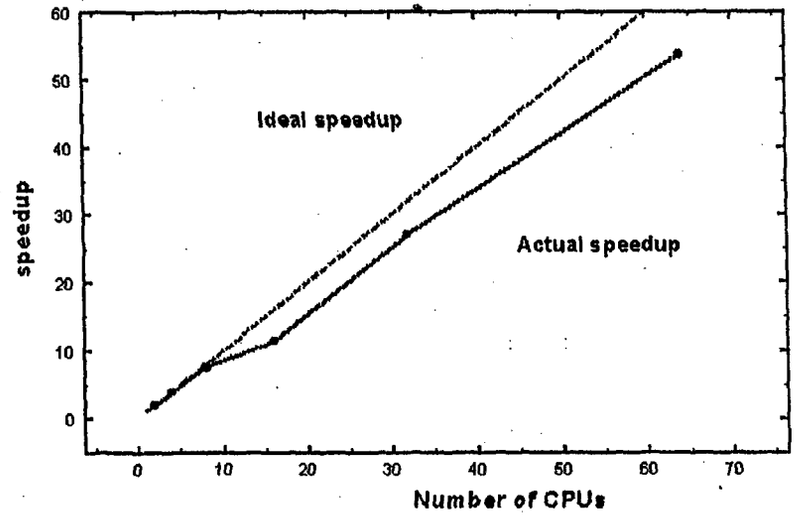


GAMESS

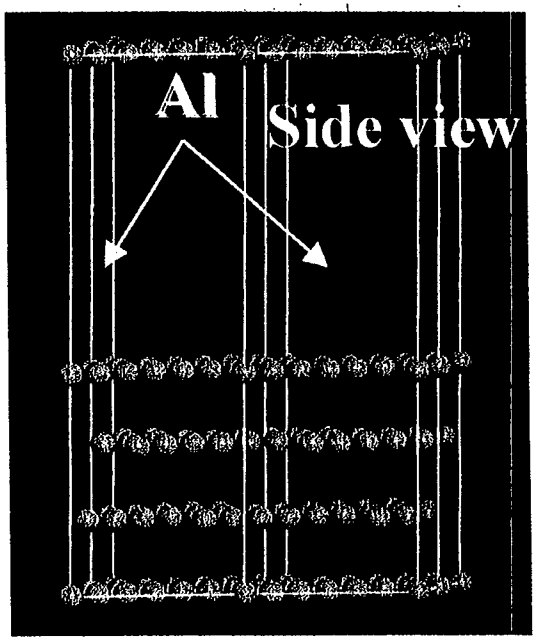


CASTEP

Run on SGI O3K

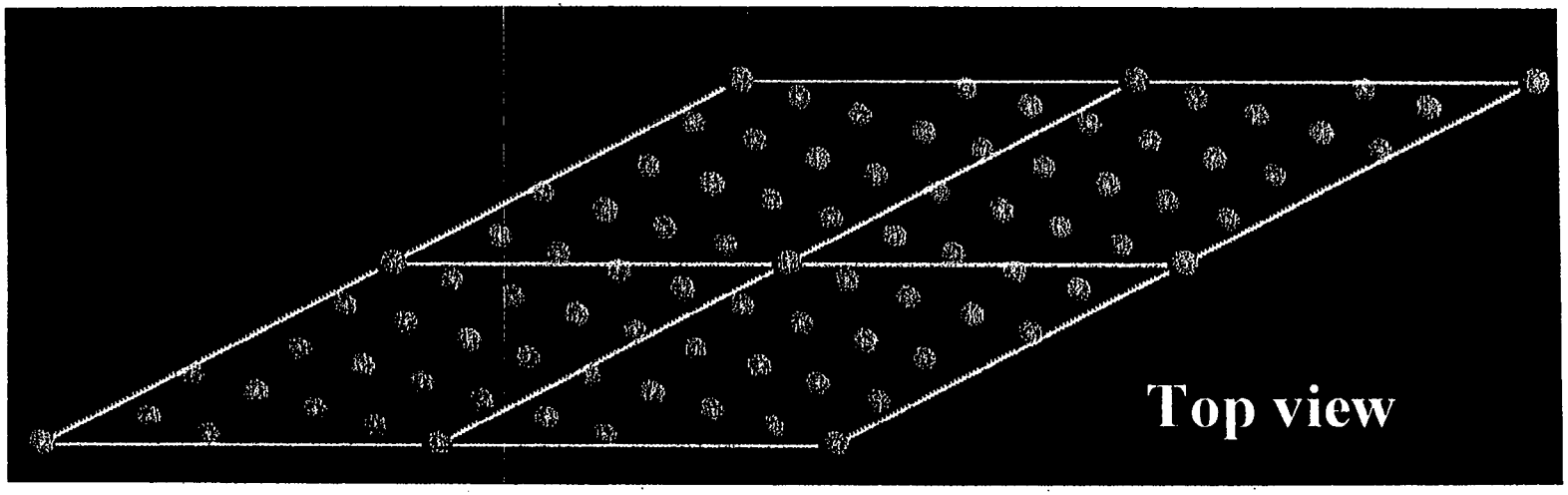


Al(111) Slab Model (I)

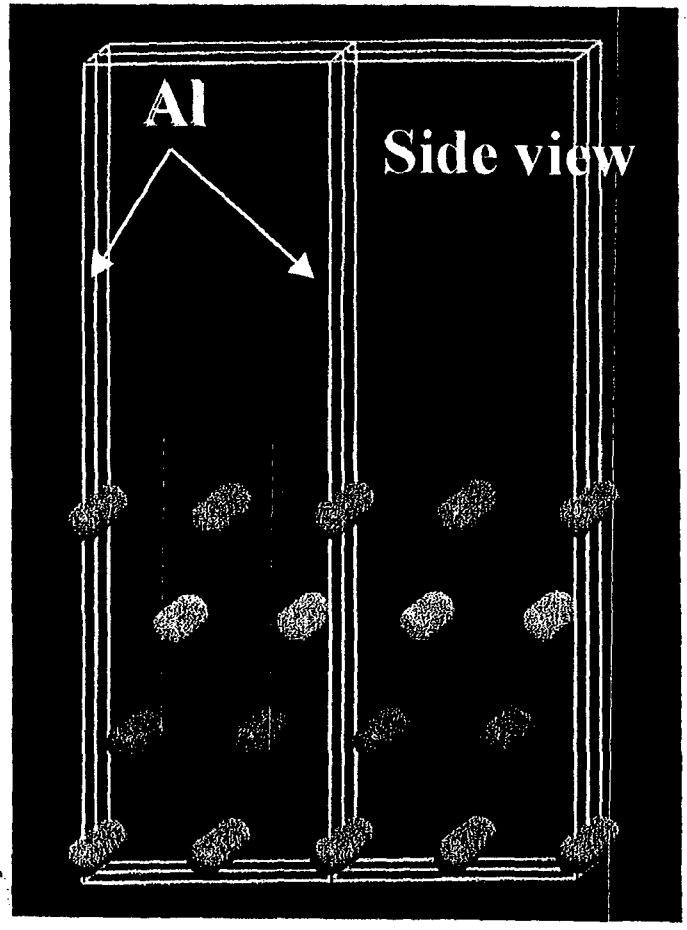


- **Two surface models have been used:** $(\sqrt{7}x\sqrt{7})R19.1°$

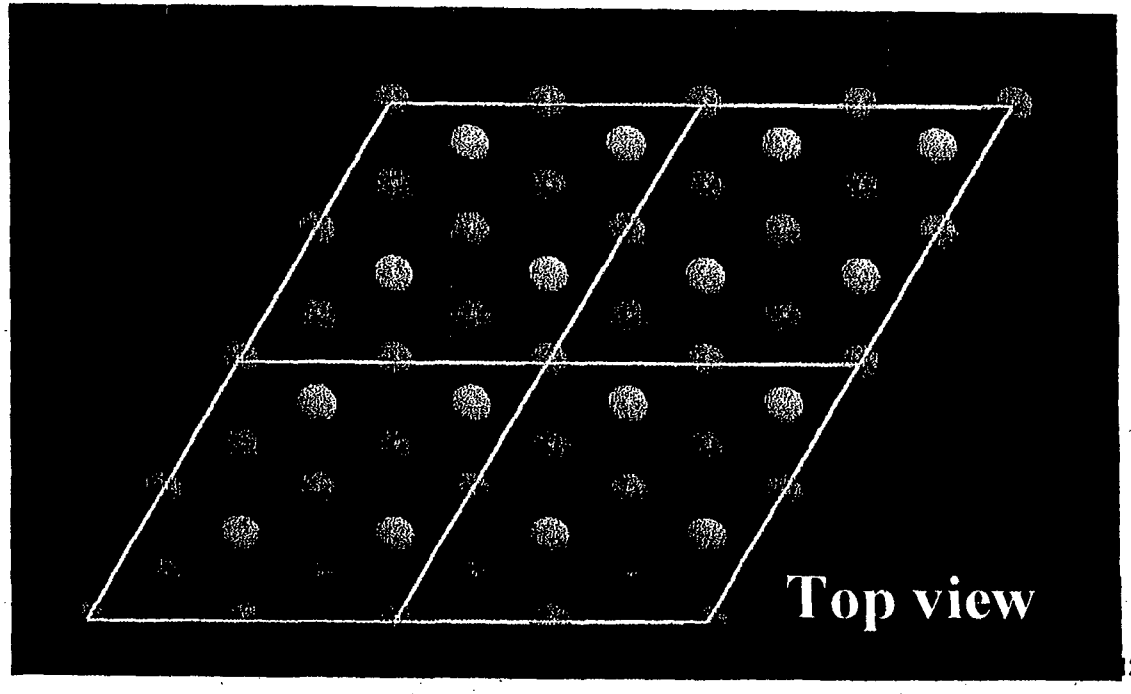
1. Al(111)-
slab model with 4 layers
(28 Al atoms) for small molecules (nitromethane)



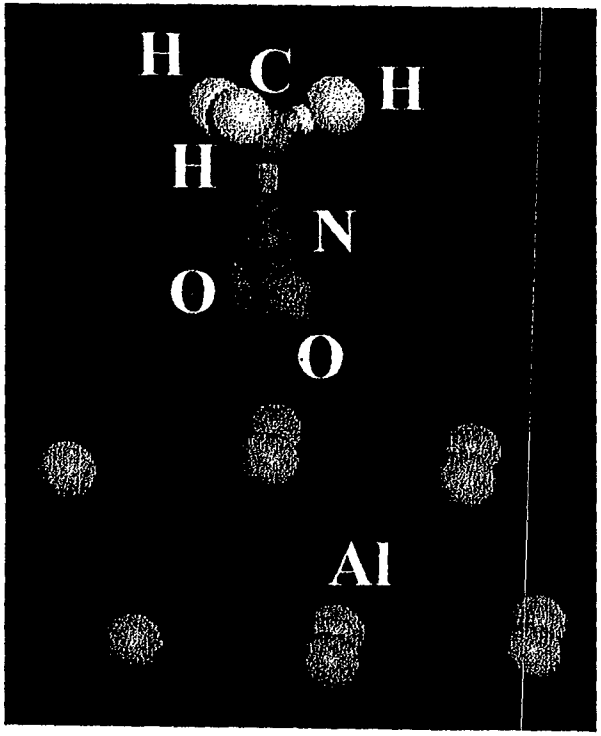
Al(111) Slab Model (II)



2. Al(111)- (3x3) surface units slab model with 4 layers (36 Al atoms) for larger molecules (FOX7, HMX)

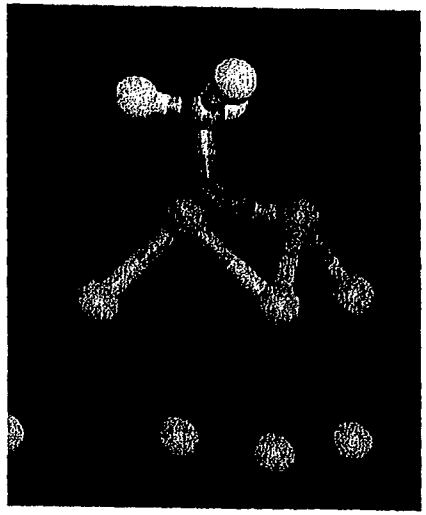


Chemisorption Properties of Nitromethane on Al(111)

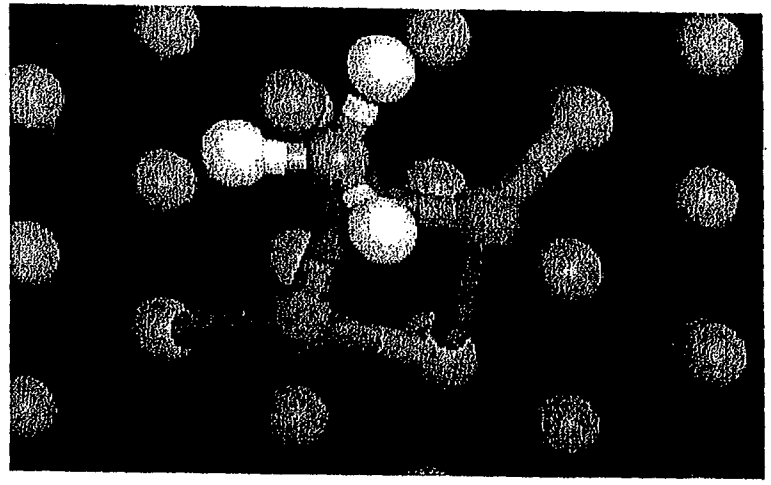


Initial configuration

Final configuration



side view

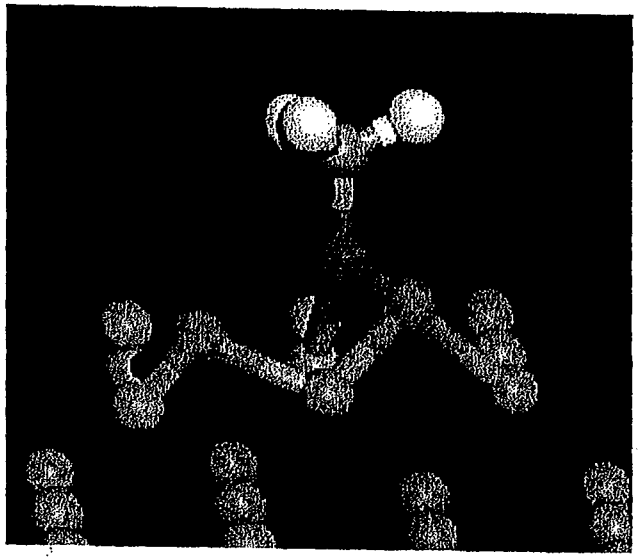


top view

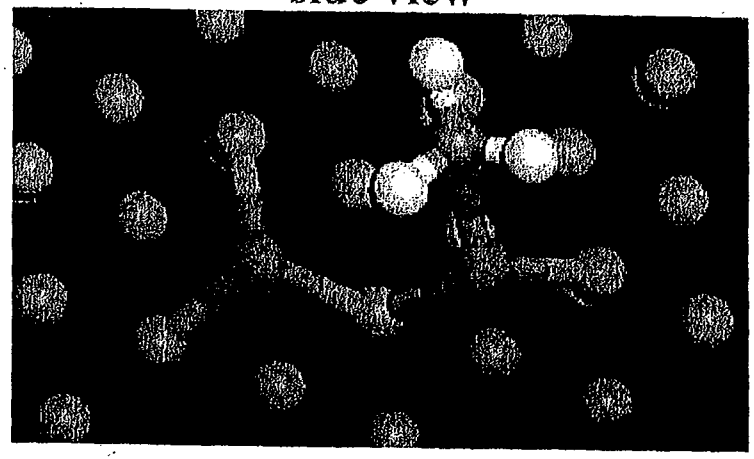
Formation of strong Al-O bonds; deformations of NM molecule

Dissociative Chemisorption of Nitromethane

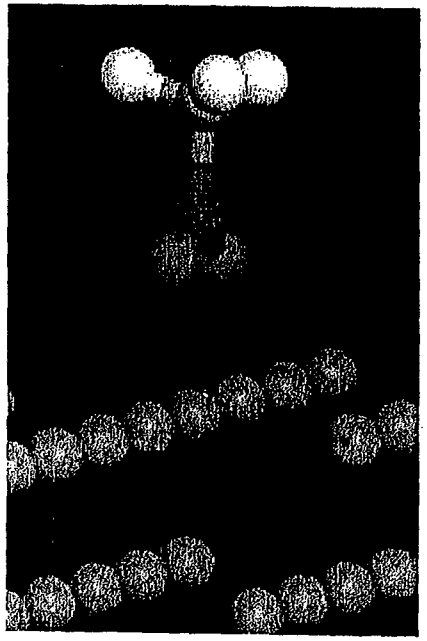
Final configuration



side view



top view

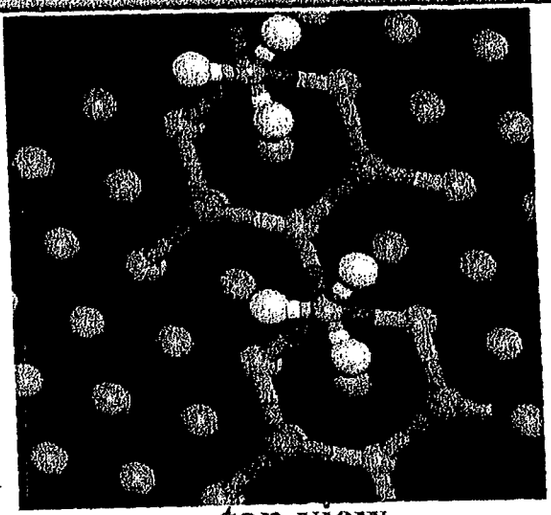


Initial configuration

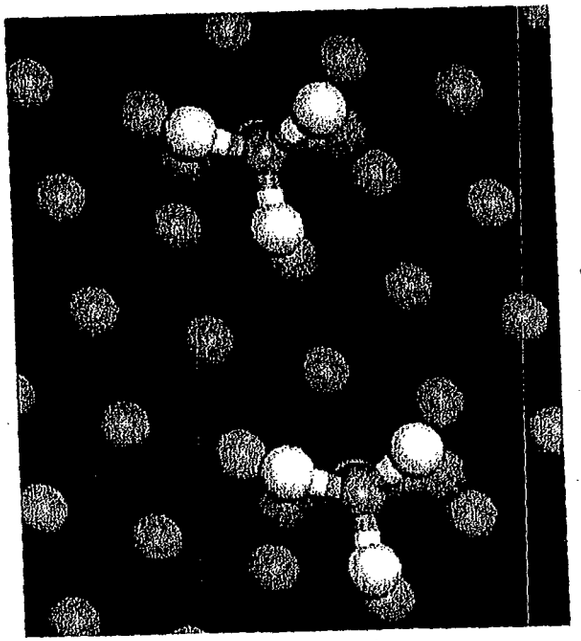
* **Dissociation of NM molecule.**
* **Oxidation of Al surface atoms.**

Dissociative Chemisorption of Nitromethane with Complete Elimination of O atoms

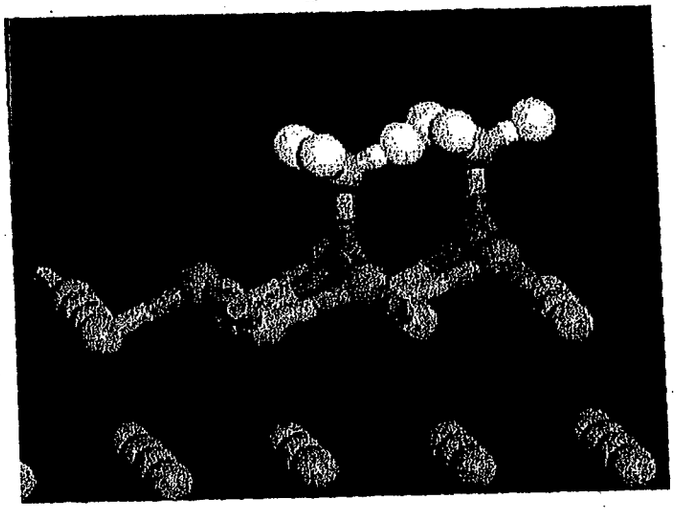
Final configuration



top view



Initial configuration

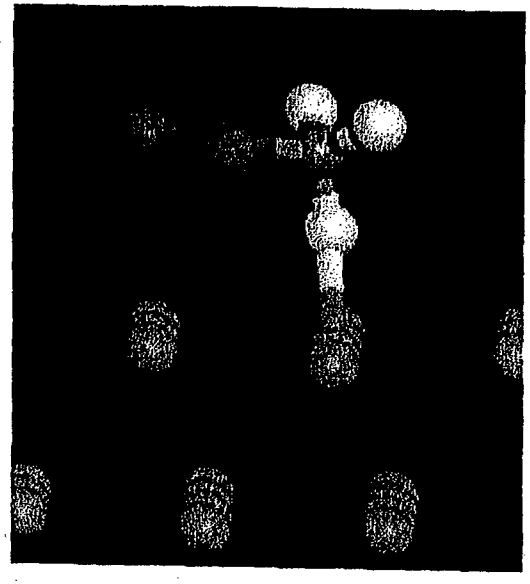


side view

***Both O atoms are eliminated.**

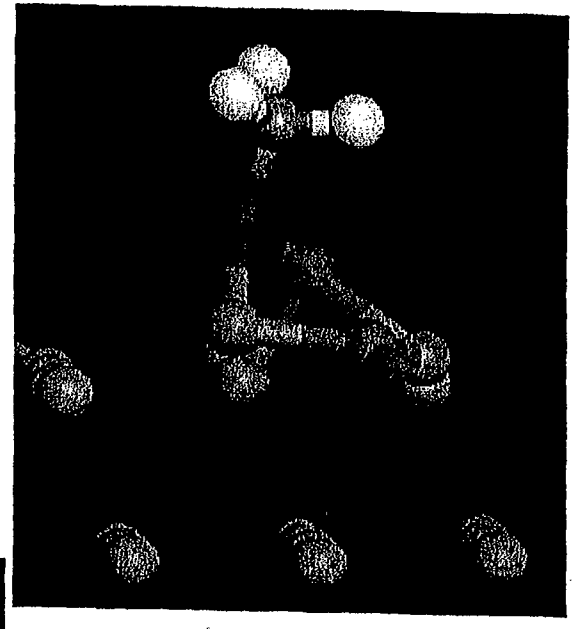
***Both O atoms contribute to oxidation of Al atoms.**

Dissociative Chemisorption of Nitromethane: Molecular Reorientation and N-O Dissociation

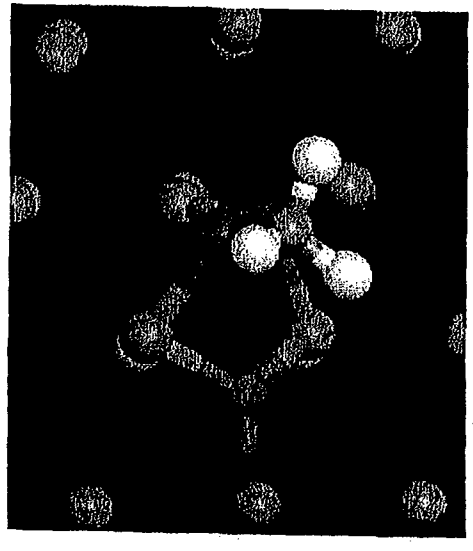


Initial configuration

Final configuration



top view

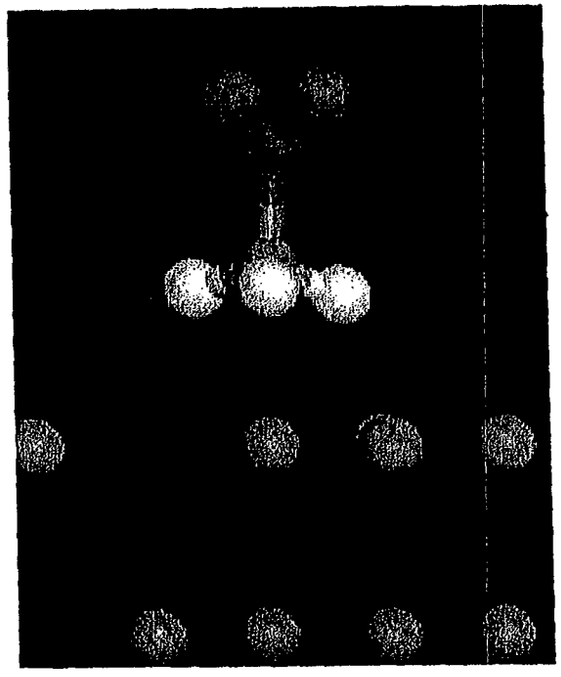


side view

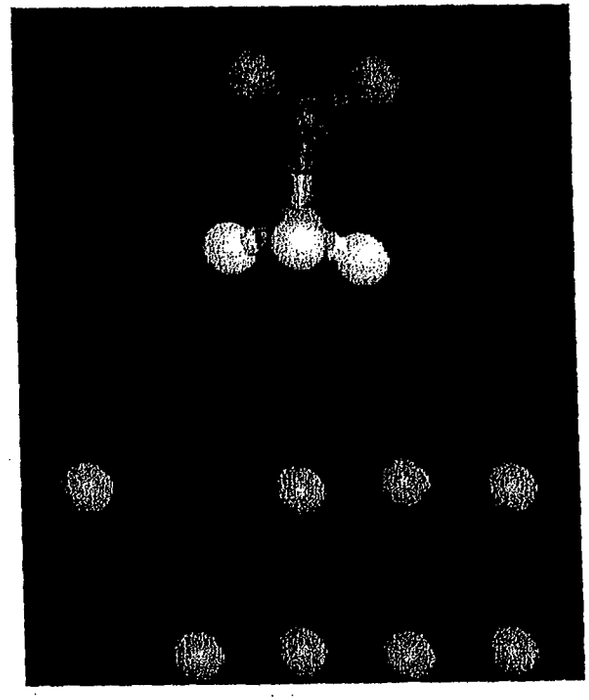
***rotation of the molecule to maximize Al-O interaction**

***N-O dissociation and formation of Al-O bonds**

There are configurations in which nitromethane can escape from being adsorbed on the surface.



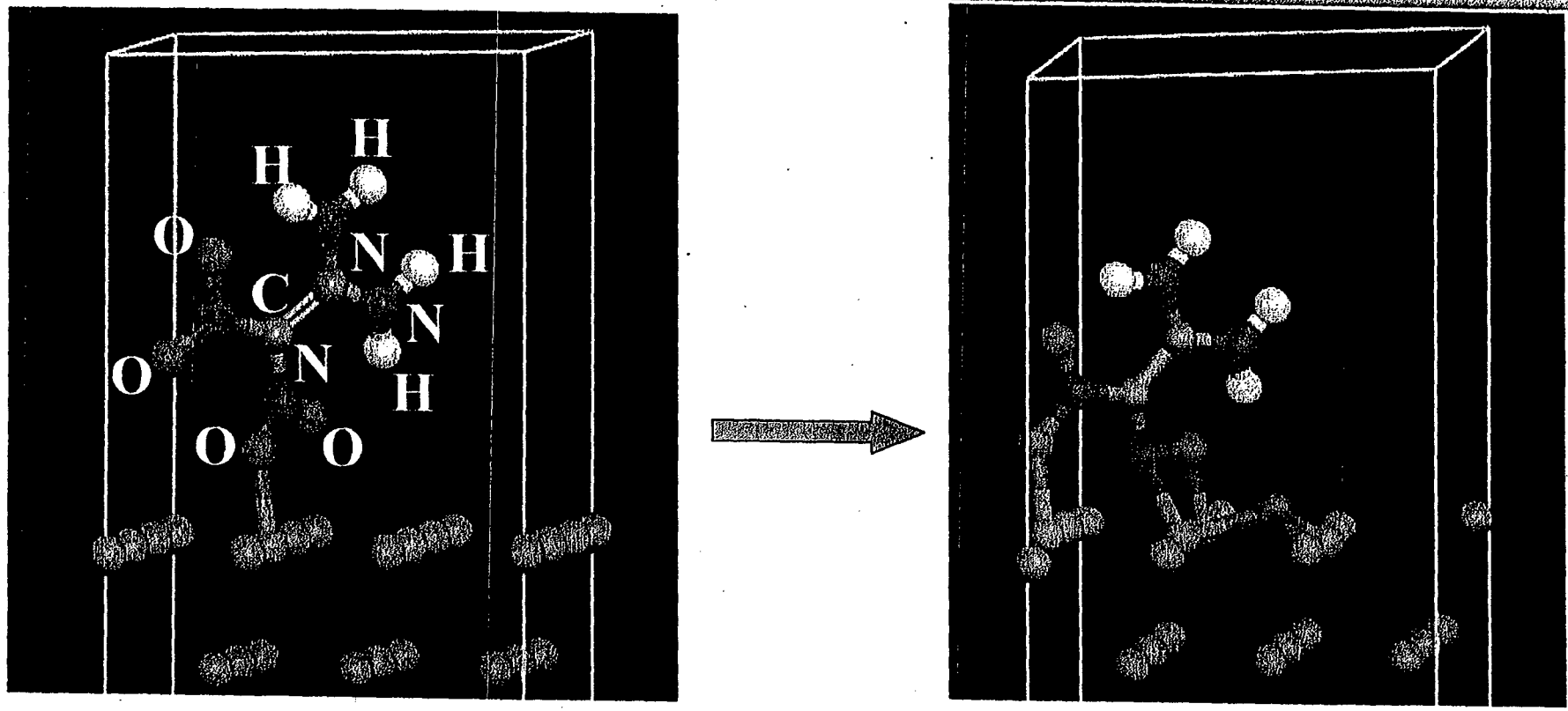
Initial configuration



Final configuration

Are these processes specific to
only polymerizing F

Chemisorption Studies of FOX7 ($C_2N_4O_4H_4$) on Al(111)



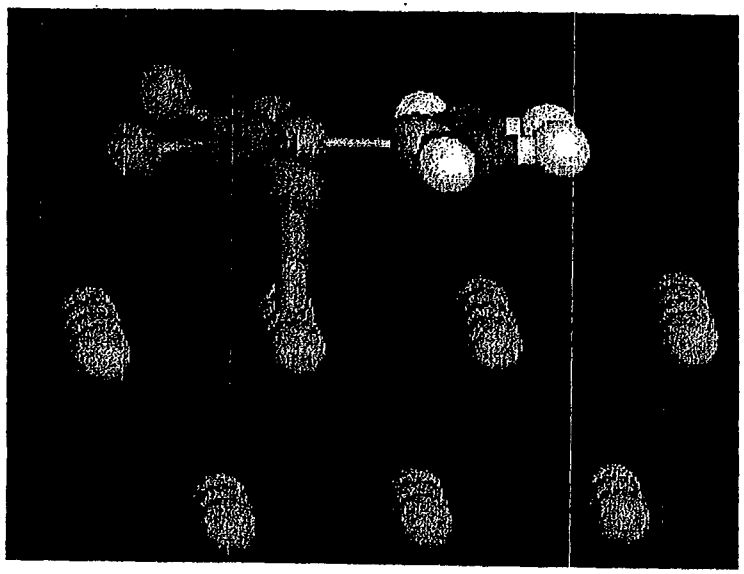
Initial configuration

Final configuration

* dissociation of N-O bonds can take place.

* O atom embeds into the lattice

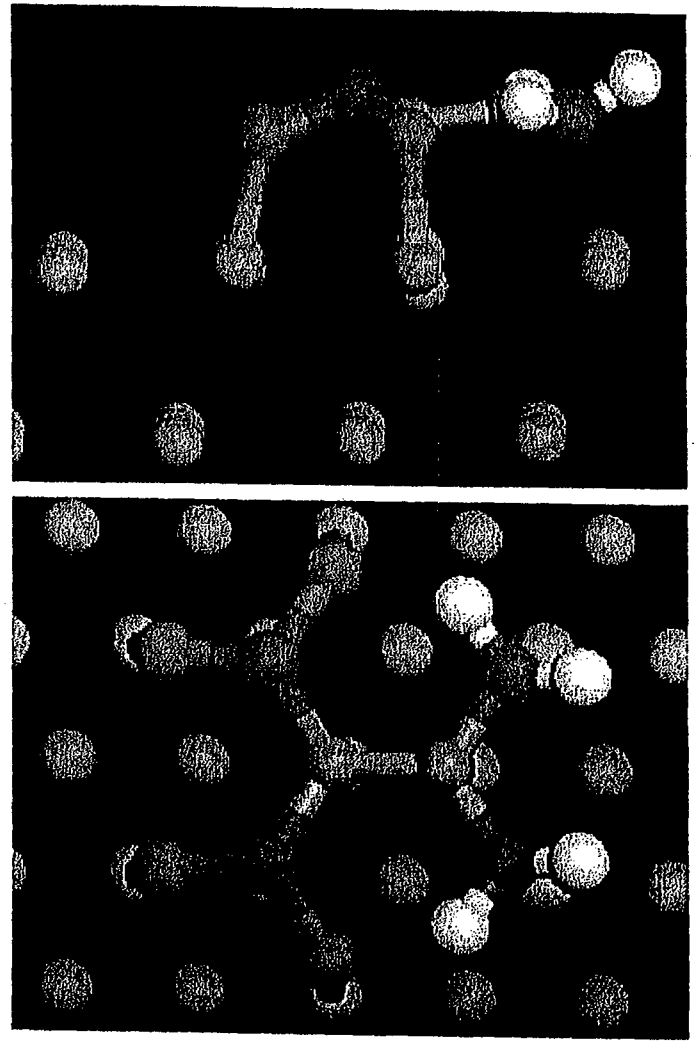
Chemisorption of FOX7 with Formation of Bridged Structures



Initial configuration

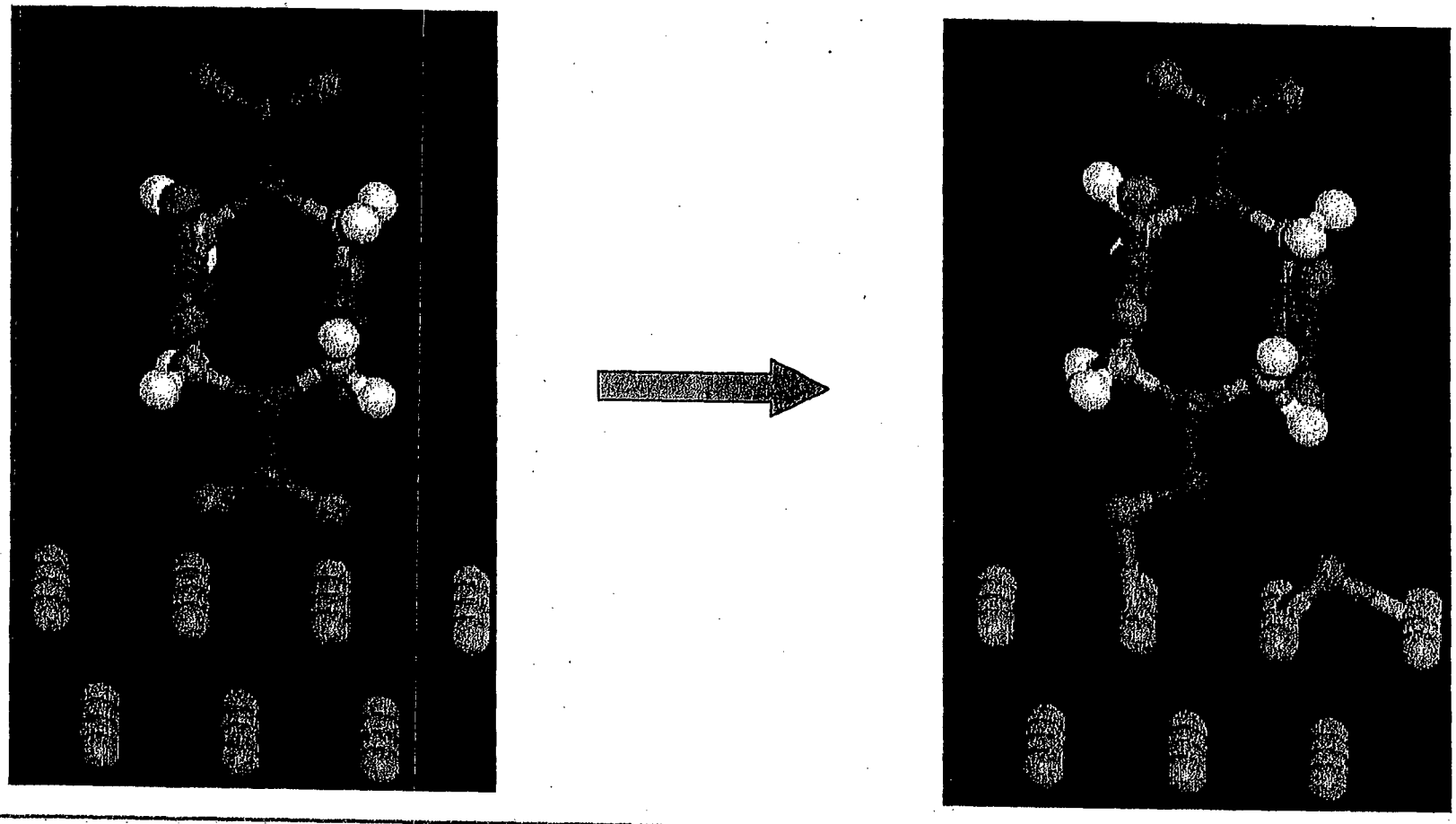
side view

top view



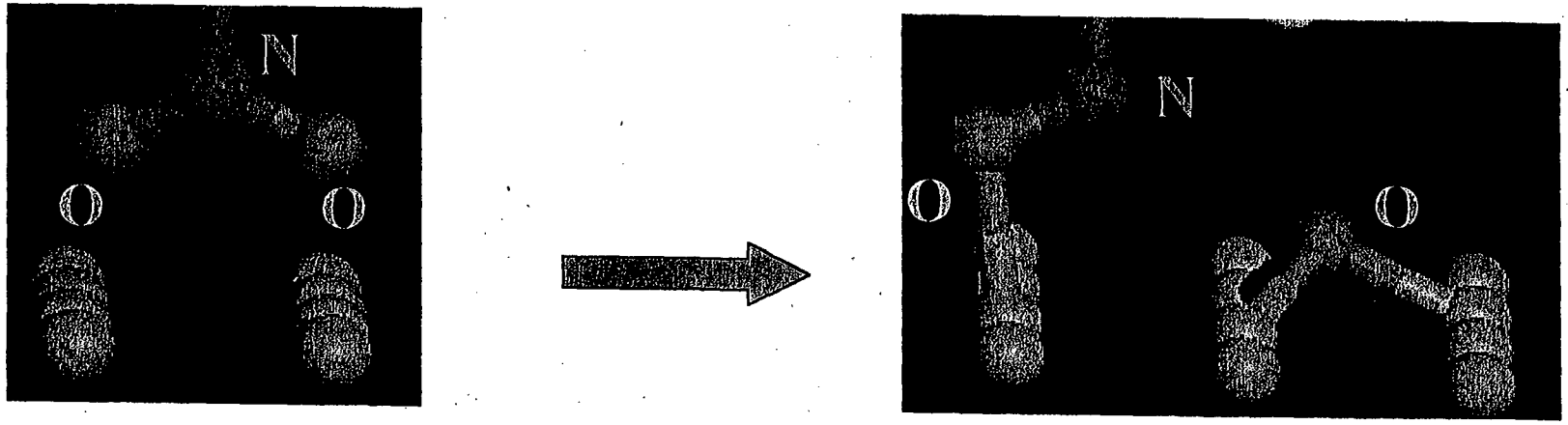
Final configuration

Chemisorption Studies of HMX ($C_4N_8O_8H_8$) on Al(111)



For HMX we observe a similar process:
dissociation of NO_2 groups with formation of Al-O bonds

Conclusions



Dissociation of NO_2 (from either C-NO_2 or N-NO_2) with formation of Al-O bonds seem to be a general process in compounds containing nitro groups.

Summary

Interactions of nitromethane, FOX-7, and HMX with the aluminum (111) surface have been calculated.

- Dissociation of one or more oxygen atoms, with subsequent chemisorption of the radical fragments on the aluminum surface, is a common mechanism for nitro-containing molecules.

- Nitro-containing molecules will not fully inhibit formation of an oxide layer on the surface of aluminum.

DOD ARL MSRC
NAVO MSRC

Acknowledgments

Financial Support

DOD HPCMP
Challenge Project Award

DOE
DURINT-ARO
AFOSR